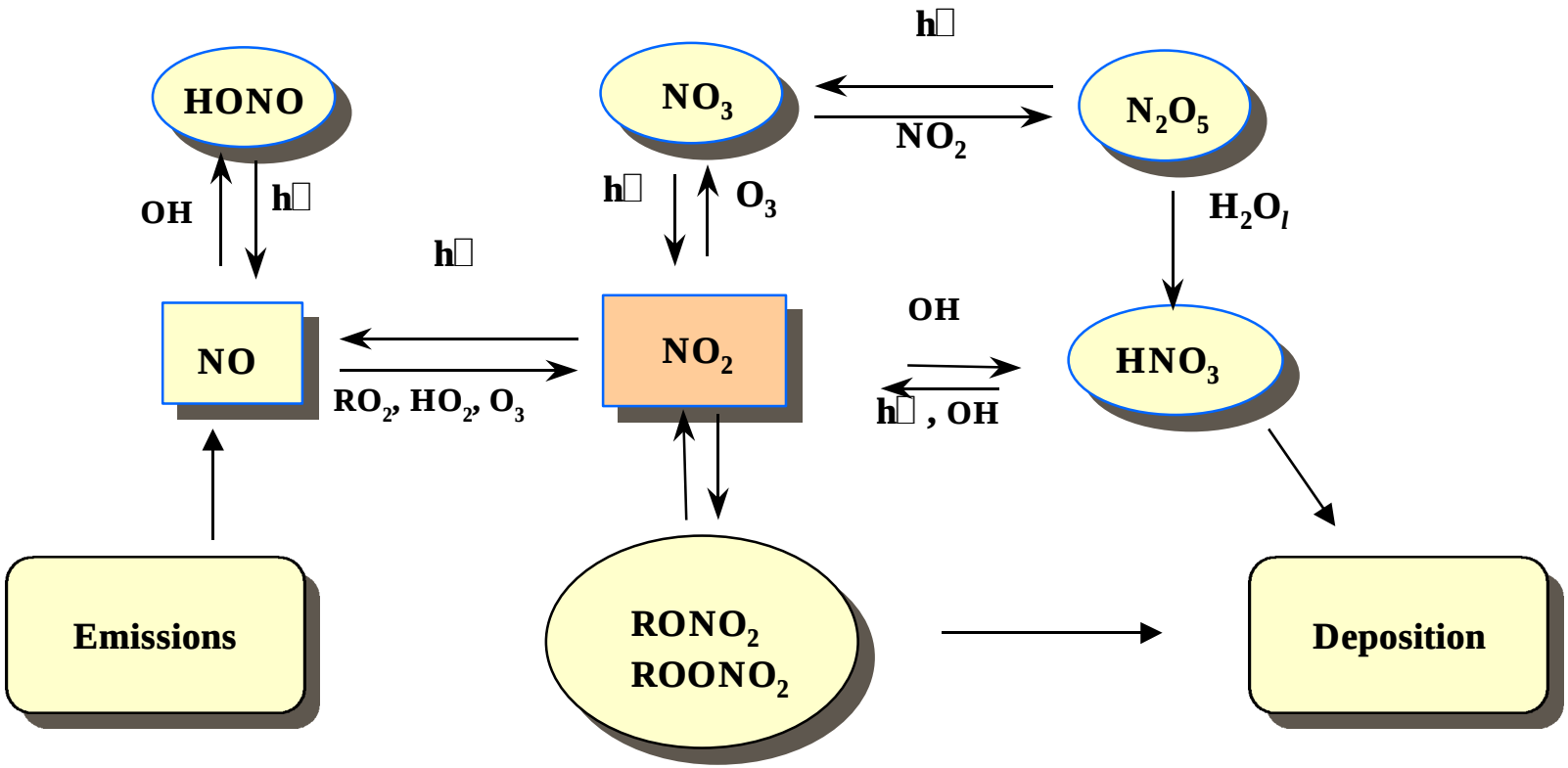
Labile NO_y Detection by Thermal Decomposition/Laser Induced Fluorescence

Douglas A. Day, Paul Wooldridge, Michael Dillon, Ronald C. Cohen
Departments of Chemistry and of Geology and Geophysics
University of California, Berkeley

This work was supported by the NASA Instrument Incubator program Contract NAS1-99053

We describe a prototype designed to obtain *in situ* observations of the concentrations of the major NO_y reservoirs. Thermal dissociation (TD) is used to fragment labile NO_y species into NO_2 and a companion radical. The NO_2 fragment is then detected by laser-induced fluorescence (LIF). The LIF instrument developed in our group is accurate (~5%), sensitive (~10 ppt / 10 seconds), precise and free from interferences. It is lightweight (as little as 200 lbs), compact, autonomous for days to months, and capable of making measurements from ground-based and airborne platforms. The TD section is a second channel operating in parallel with a channel detecting ambient NO_2. In the TD channel, ambient air flows rapidly (1.5 s residence time) through a quartz tube heated by a nichrome wire. NO_y species that fragment to NO_2 are then detected by LIF. Calculations and laboratory experiments show the instrument can easily distinguish between signals due to N_2O_5, peroxynitrates (RO_2NO_2), and alkyl nitrates and hydroxy nitrates ($RONO_2$), and HNO_3 by varying the temperature in the dissociation region. A laboratory intercomparison between a NO_y chemiluminescence detector and the TD/LIF technique showed excellent agreement for samples of n-propyl nitrate. Details of the laboratory tests and of an ambient field trial will be presented.

NO_y Photochemistry



Why a new technique?

- N_2O_5 and HNO_4 have never been measured *in situ*. N_2O_5 is an important path for loss of NO_x through heterogeneous conversion to HNO_3 in both the stratosphere and troposphere.

- The extent to which NO_x emission can lead to ozone production downwind of sources is affected by the partitioning of NO_x between soluble and insoluble reservoir species.

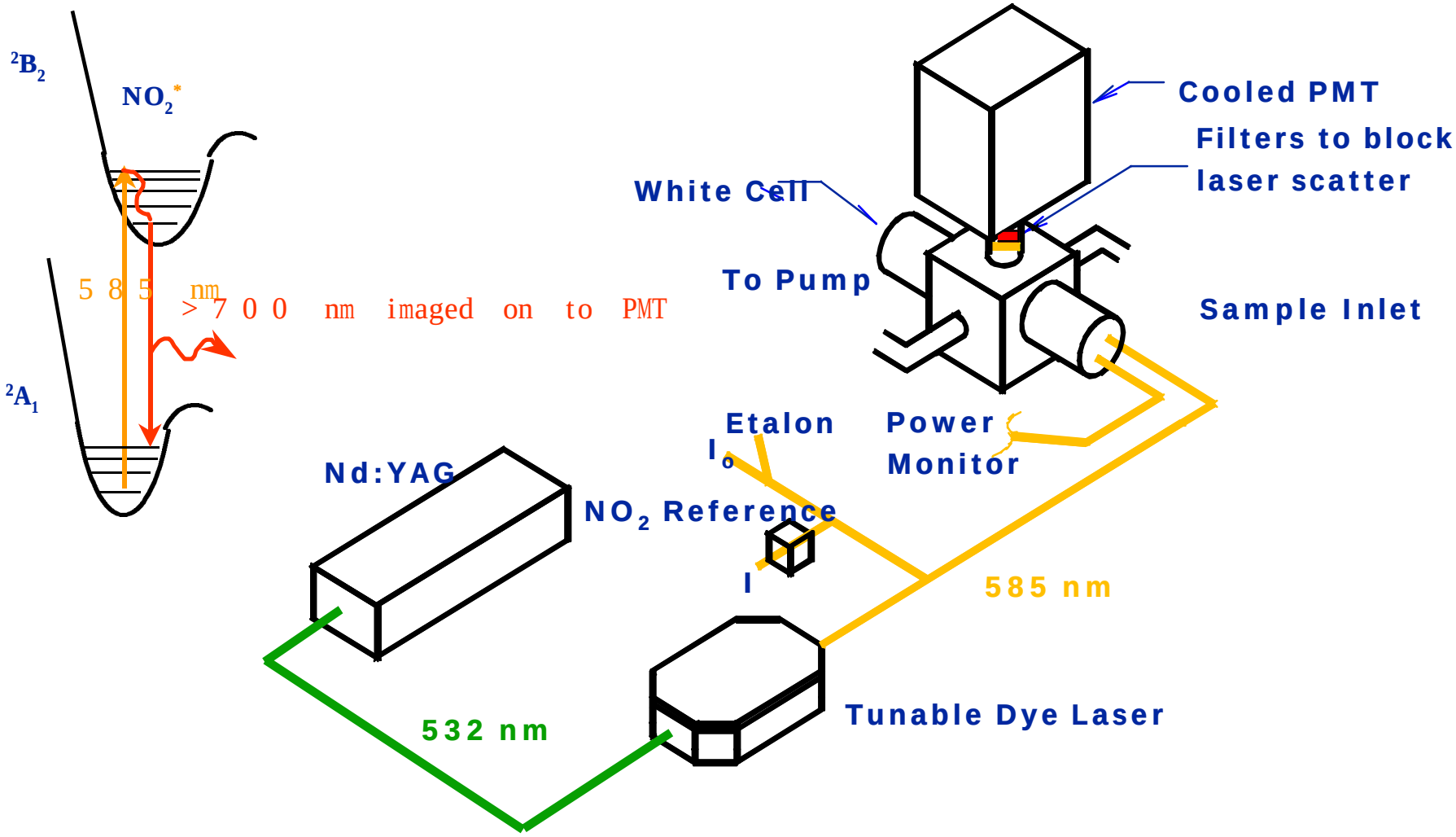
- Missing NO_y: Often found that the sum of individually speciated NO_y (NO, NO_2, PAN, HNO_3) do not add up to the total NO_y measured separately. Missing NO_y is often correlated with degree of processing suggesting importance of a slew of organic nitrates: alkyl nitrates, hydroxy nitrates, other peroxynitrates's.

- Important to measure speciated NO_y in order to assess anthropogenic vs biogenic contribution to nitrate formation.

- Existing techniques for RO_xNO_2 all use chromatography which is slow and may suffer from surface losses.

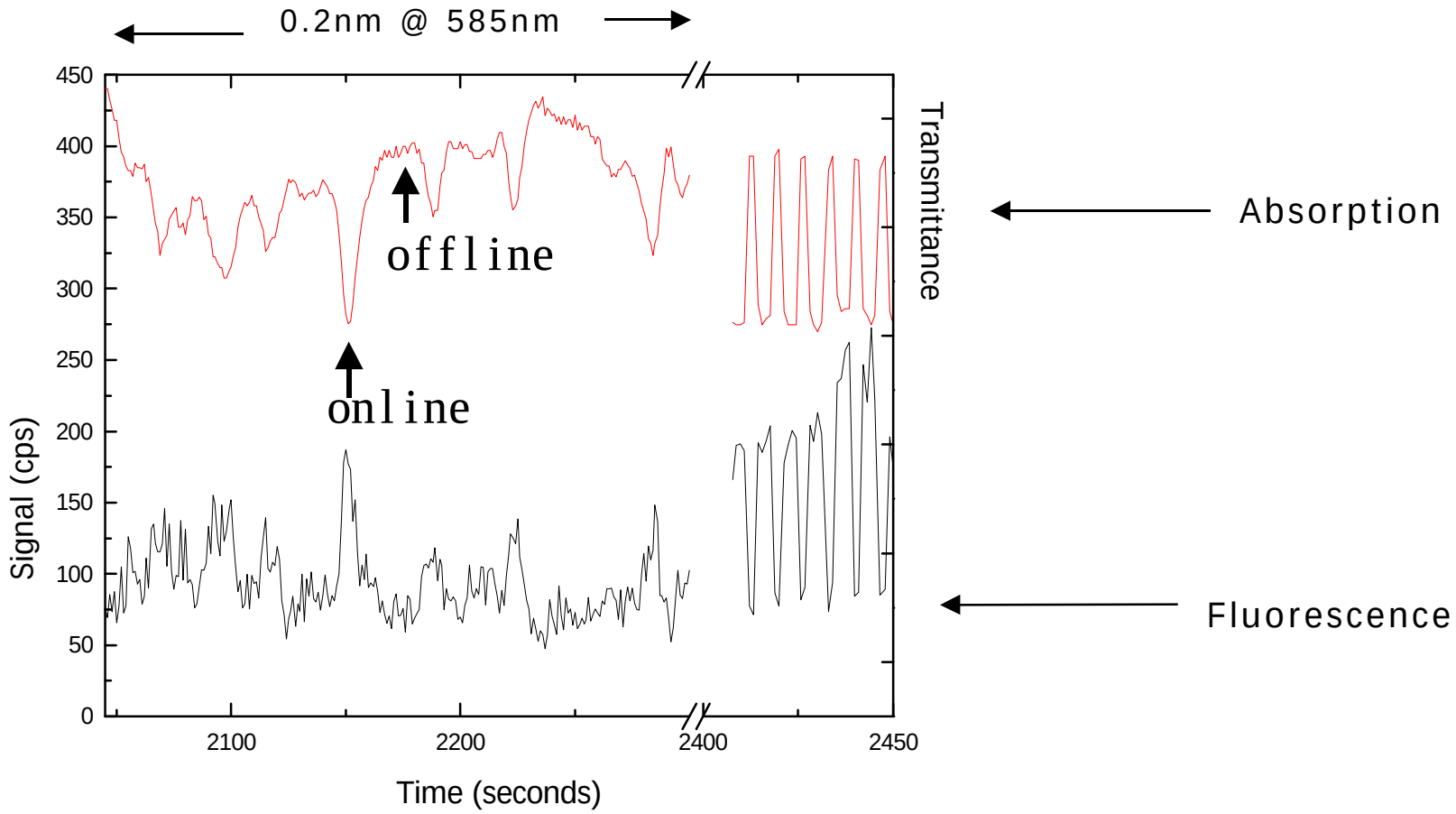
- HNO_3 is a difficult molecule to measure accurately due to inlet losses.

LIF detection of NO_2



Using a pulsed, tunable dye laser, a specific rovibronic transition of NO_2 is excited in a multipass white cell and the fluorescence is detected after physical and time-gated filtering using a PMT

The NO_2 Spectrum: Specificity



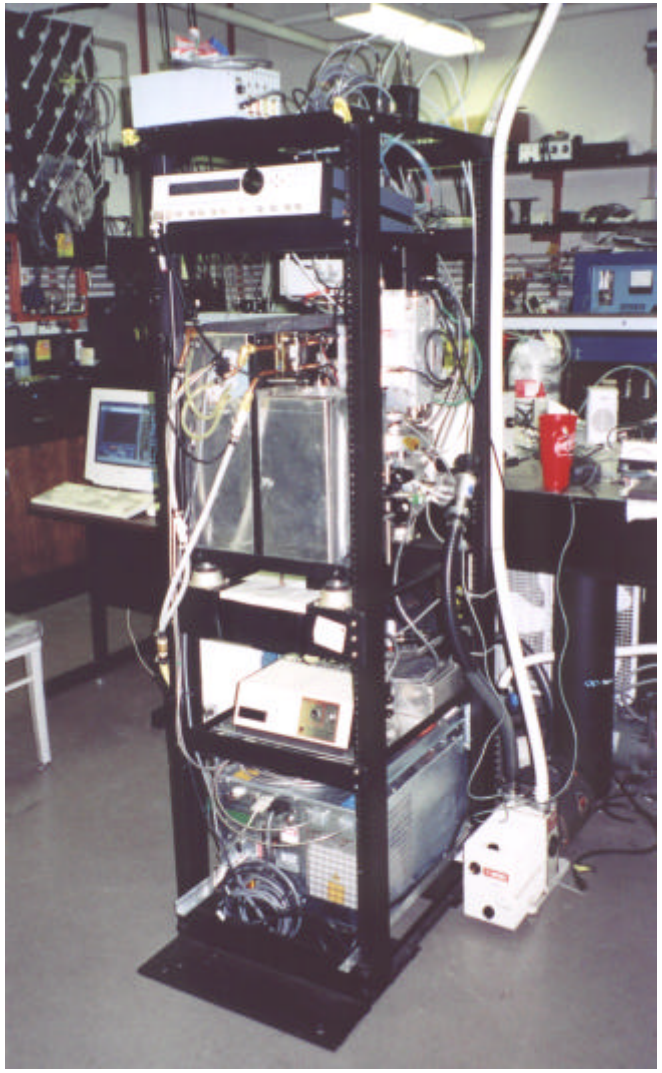
The absorption of NO2 is monitored in a reference cell (red). After tuning to the peak, the dye laser continually dithers on and off of a chosen spectral feature to demonstrate an interference-free fluorescence signal (black).

LIF NO_2: 1999

Current Status

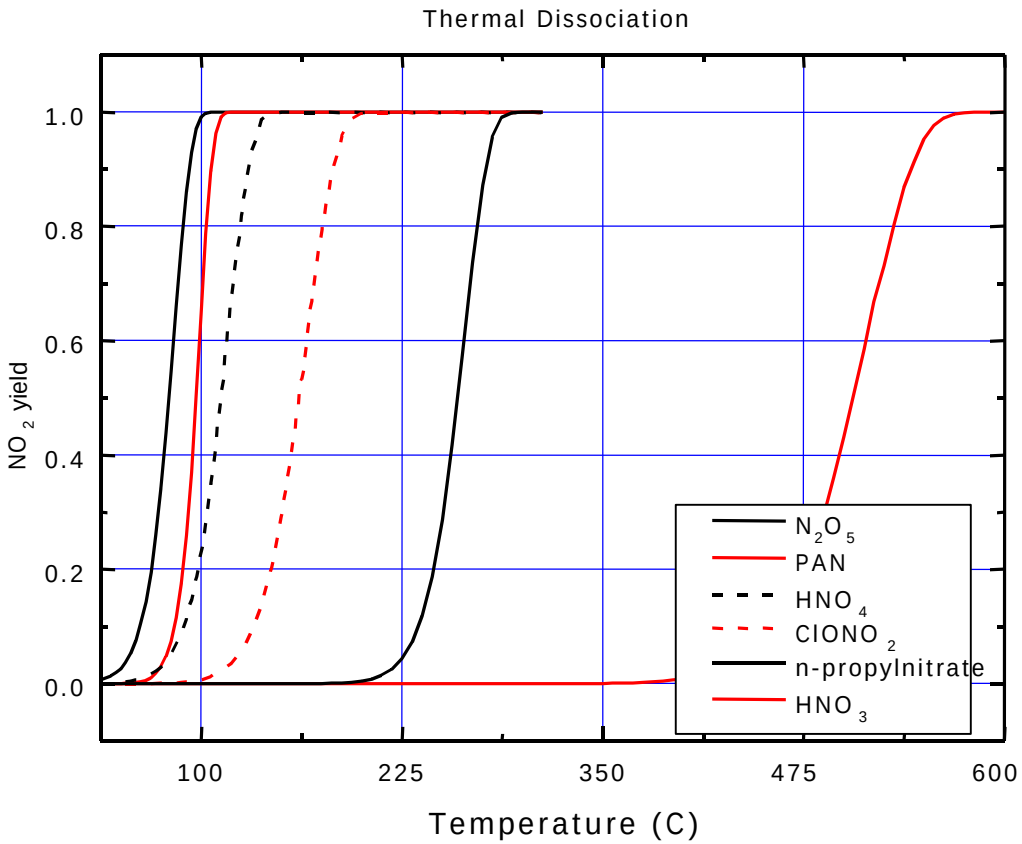
- Direct and spectroscopically specific
- accurate: □5%, 1
- sensitive: 10ppt/10sec, S/N=2
- detection limit 1ppt
- continuous and autonomous operation for more than a month
- 450lbs 3kW

Details are available in:
Thornton, Wooldridge and Cohen, Analytical Chemistry, in press, 2000



Thermal Dissociation-LIF

XNO_2 + heat → X + NO_2

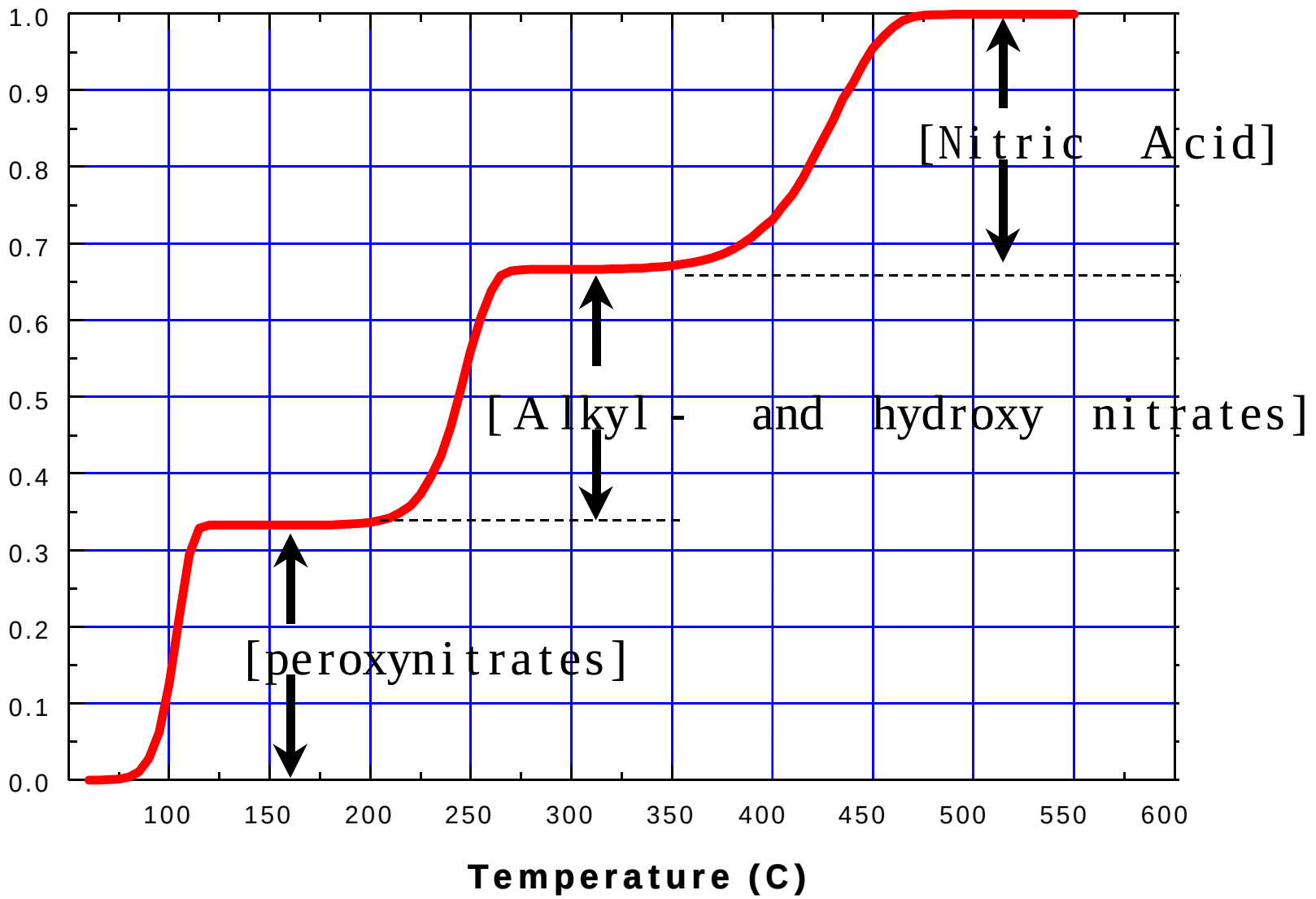


The predicted NO_2 yield vs. temperature curves for the different classes of nitrates compounds is unique

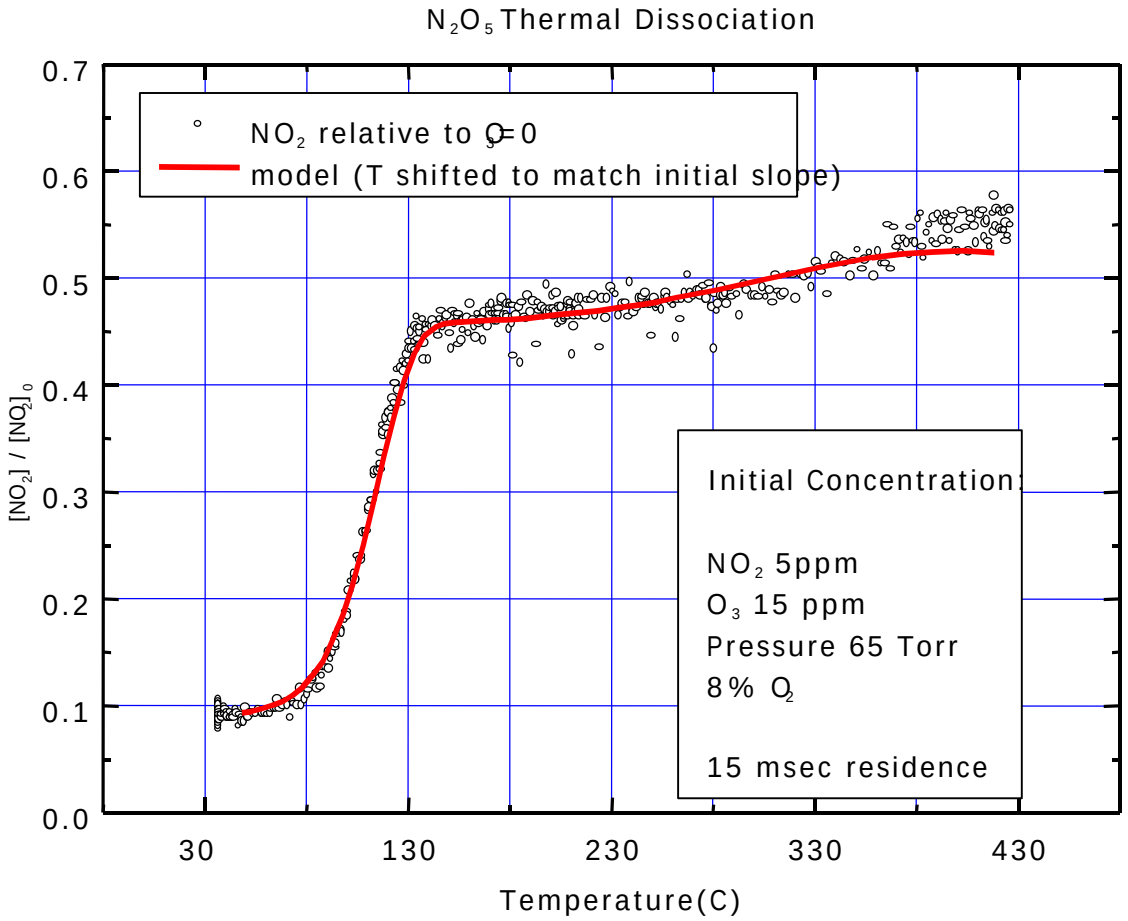
T< 50C NO_2
(1) T~ 130C N_2O_5+RO_2NO_2 +(1) (2)
T~ 300C $RONO_2$ +(2) (3)
T~ 550C HNO_3+(3) (4)

The sampled air passes immediately through a heated quartz tube where, depending up the set tem only certain classes of compounds are pyrolyzed producing NO_2 and a sister radical. The sample is transported to the detection axis via PFA tubing where the NO_2 is measure by laser induced fluoresc

NO_2 yield occurs in three easily resolved steps



N_2O_5



A simple extremely well calibrated test:

a) Measure NO_2

b) Add O_3

$NO_2 + O_3 \rightarrow NO_3 + O_2$

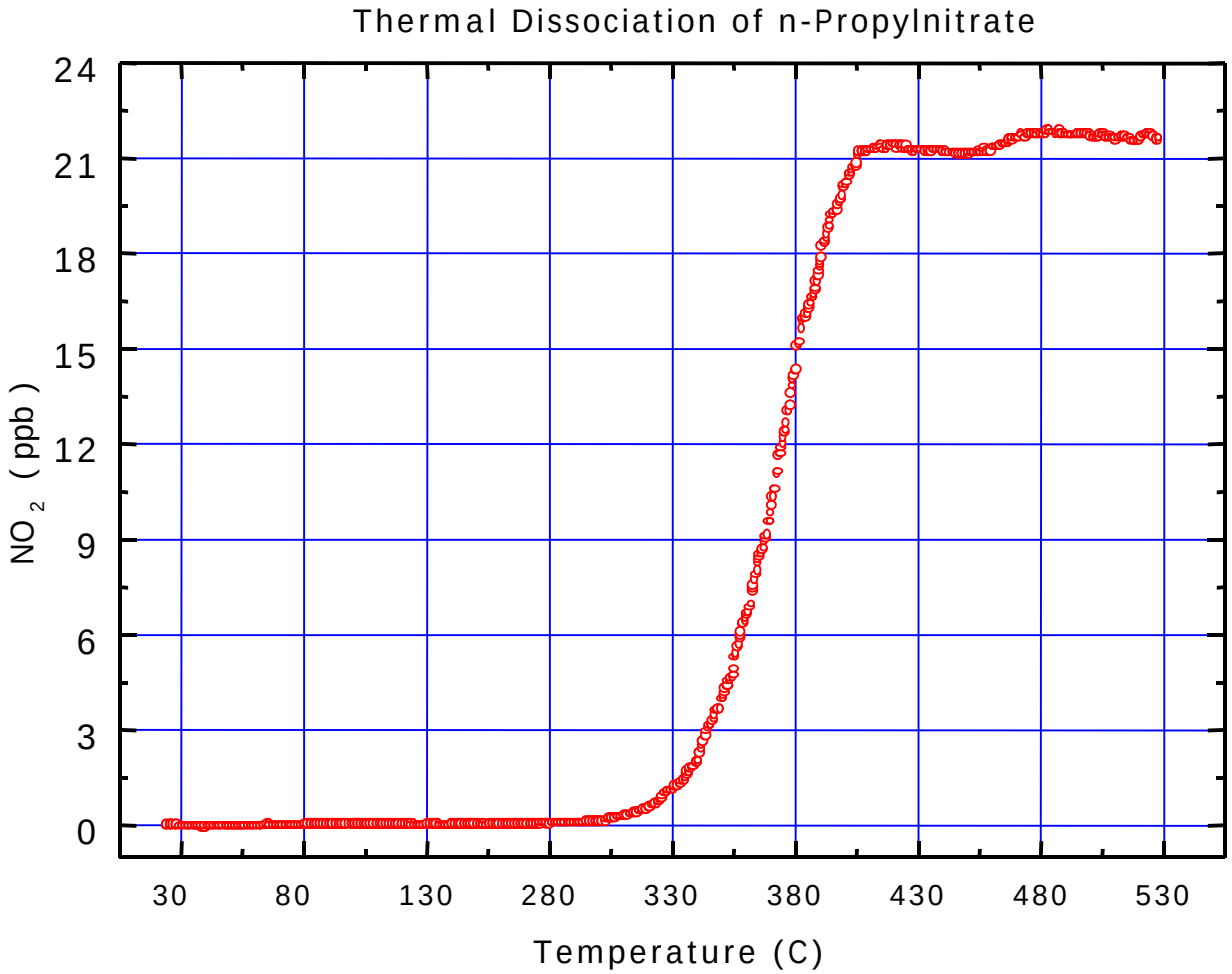
$NO_2 + NO_3 \rightarrow N_2O_5$

c) Add heat

$N_2O_5 + heat \rightarrow NO_2 + NO_3$

d) One half the original N_2O_5 is recovered as NO_2

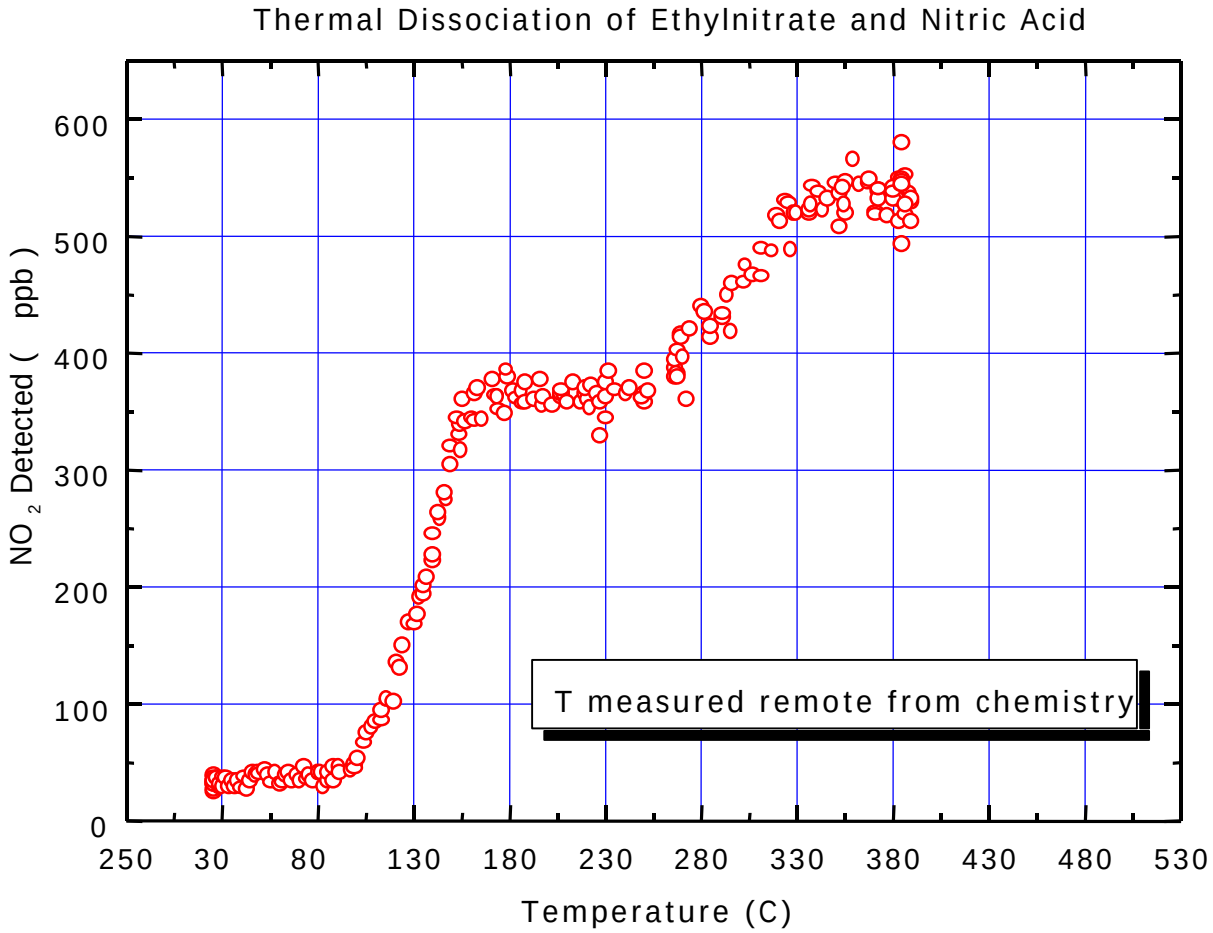
n-propylnitrate



The thermal spectrum of n-propylnitrate is observed as predicted from theory.

The vapor pressure of NPN is not know well enough to use it as a calibration standard.

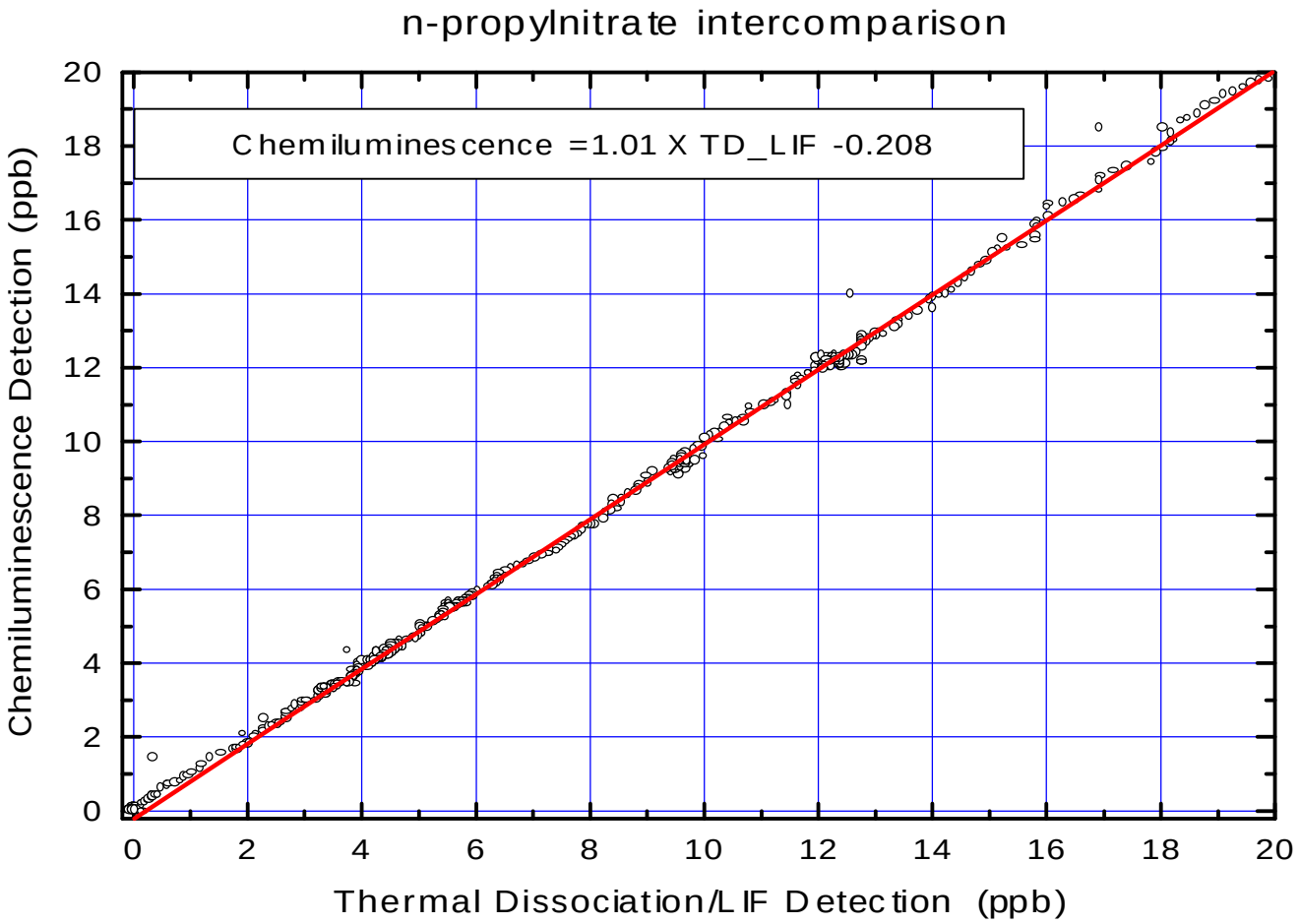
HNO_3 and $C_2H_5NO_3$



Individual compounds can be detected within mixtures.

In practice we have 2 or 3 channels set at different temperatures to record, for example, NO_2, RO_2NO_2 and HNO_3.

Intercomparison with an NO_y sensor



Two completely independent techniques give the same result over a decade of concentration.

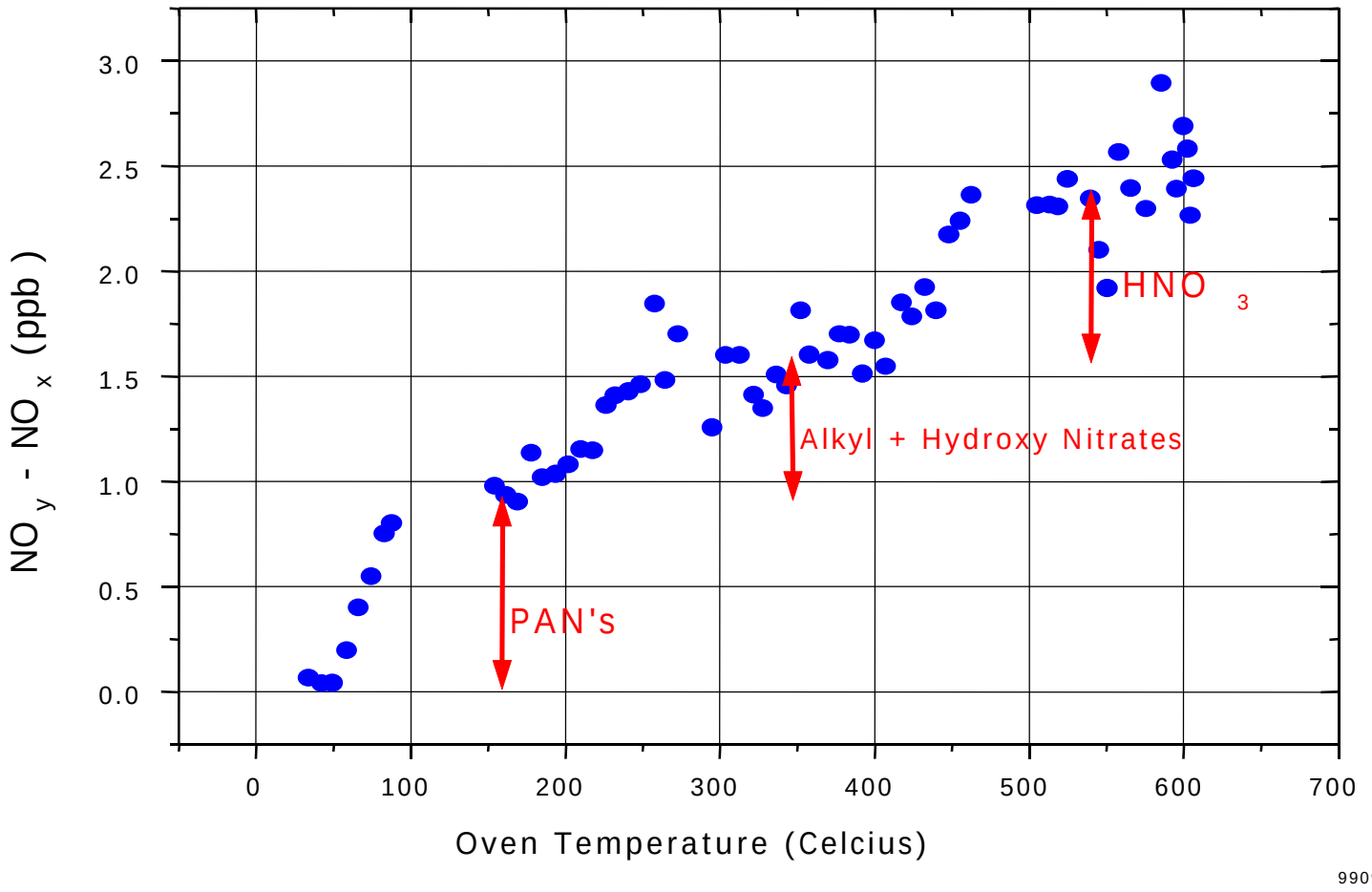
Field Trial at Blodgett Forest

- Site is a ponderosa pine plantation in the foothills of the Sierra Nevada mountains downwind from the polluted Sacramento Valley

- Prevalent biogenic emissions mixed with a NO_y rich urban plume are ideal for investigating the processes that lead to formation of organic nitrates.

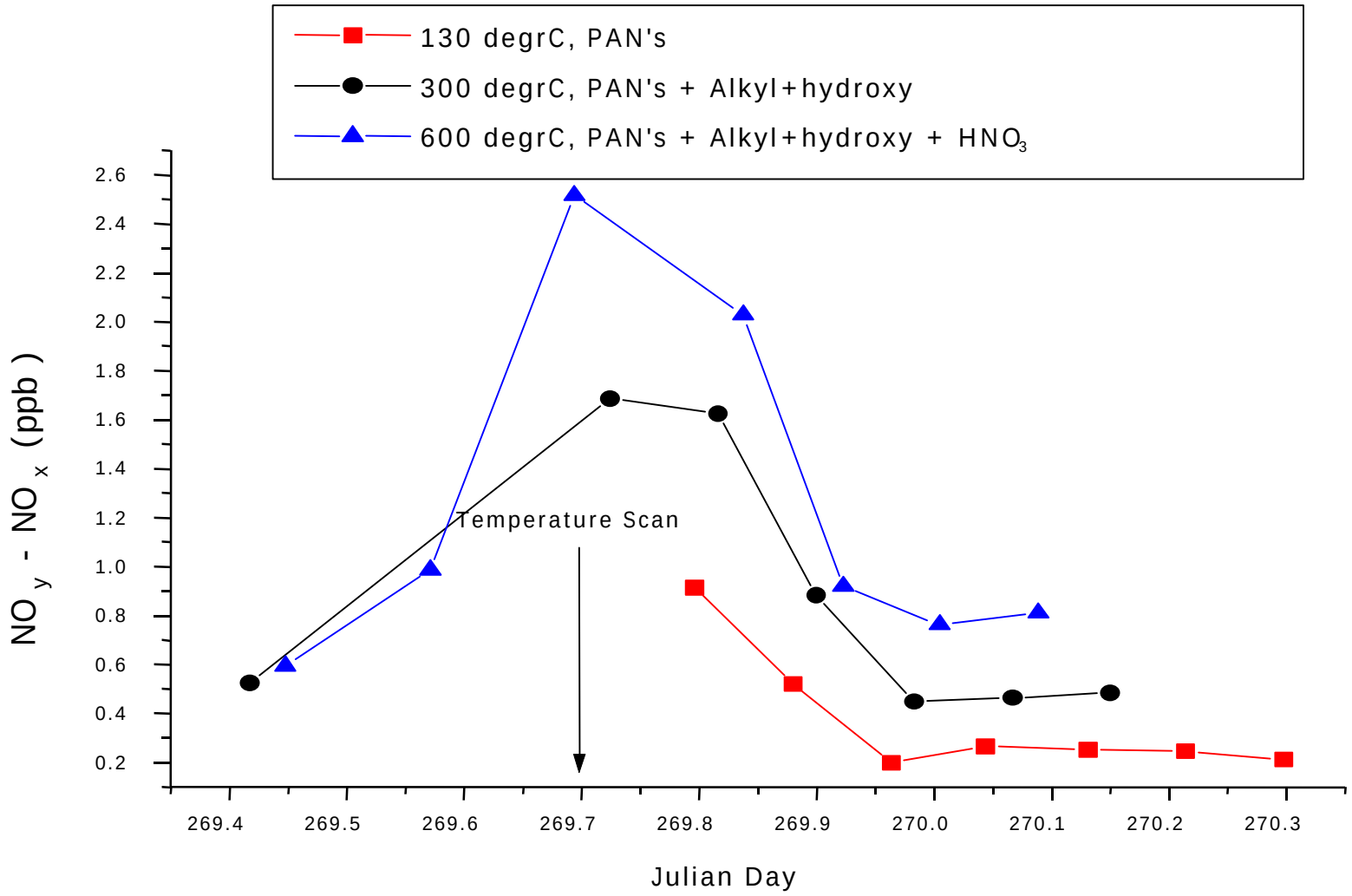
- At Blodgett Forest, peroxynitrates typically composed ¼ of the NOy and the alkyl nitrate + hydroxy nitrate group was also about ¼.

Thermal Spectrum: 990927

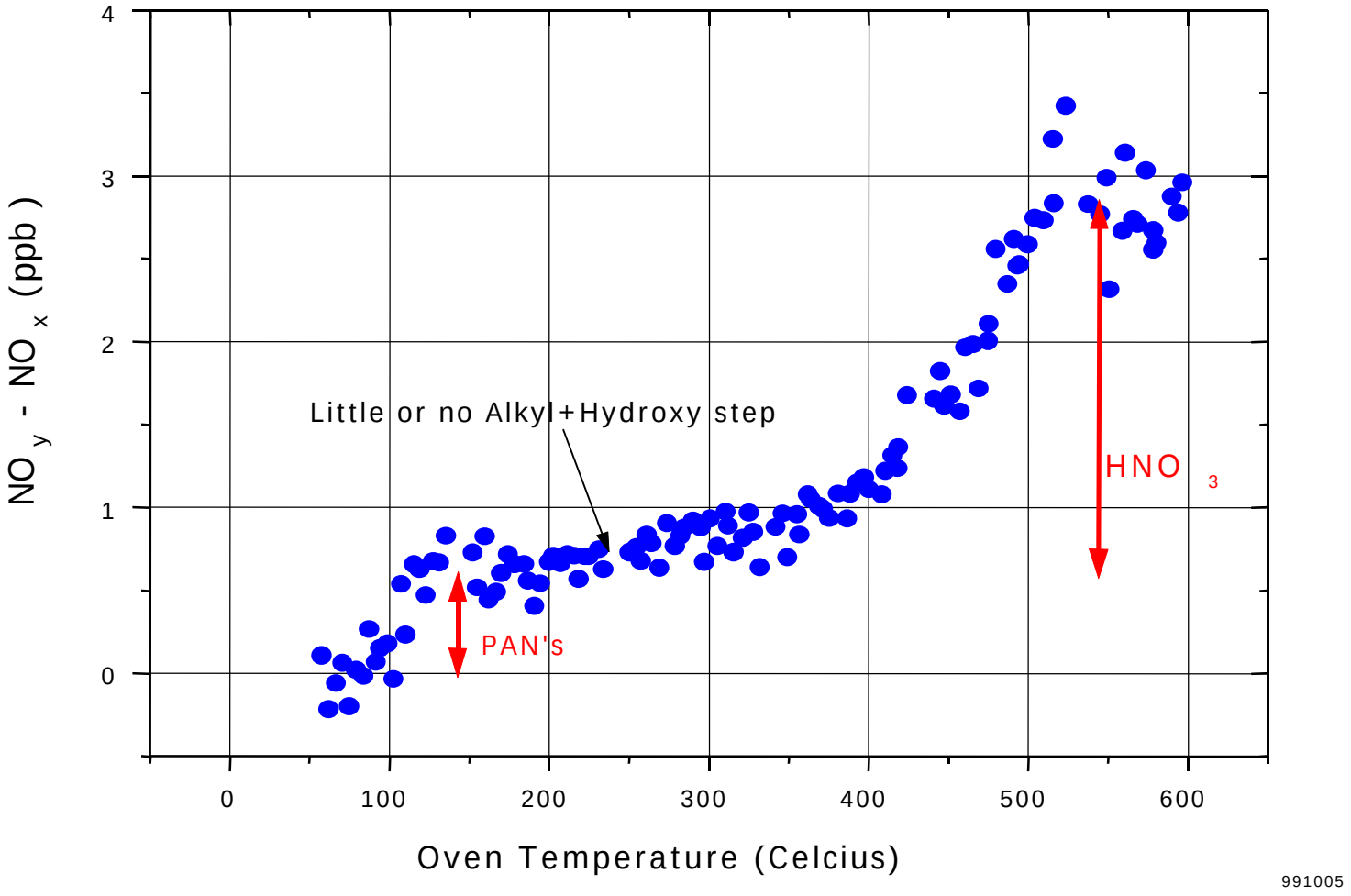


This scan was obtained in the early evening in the peak of the urban plume at Blodgett Forest at the point indicated in the slide below.

990927

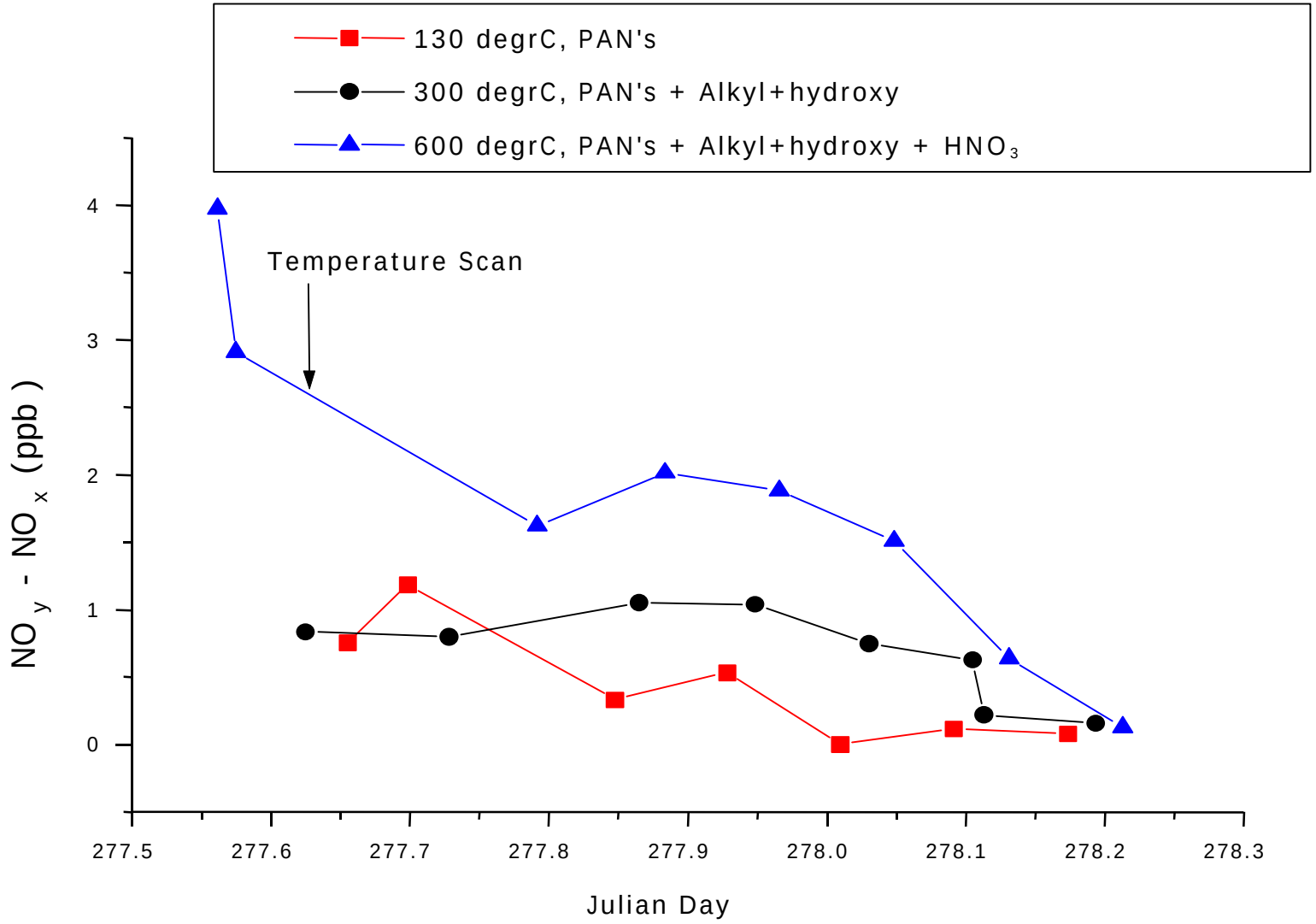

130 degrC, PAN's
300 degrC, PAN's + Alkyl+hydroxy
600 degrC, PAN's + Alkyl+hydroxy + HNO3
NOy - NOx (ppb)
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Temperature Scan
269.4
269.5
269.6
269.7
269.8
269.9
270.0
270.1
270.2
270.3
Julian Day

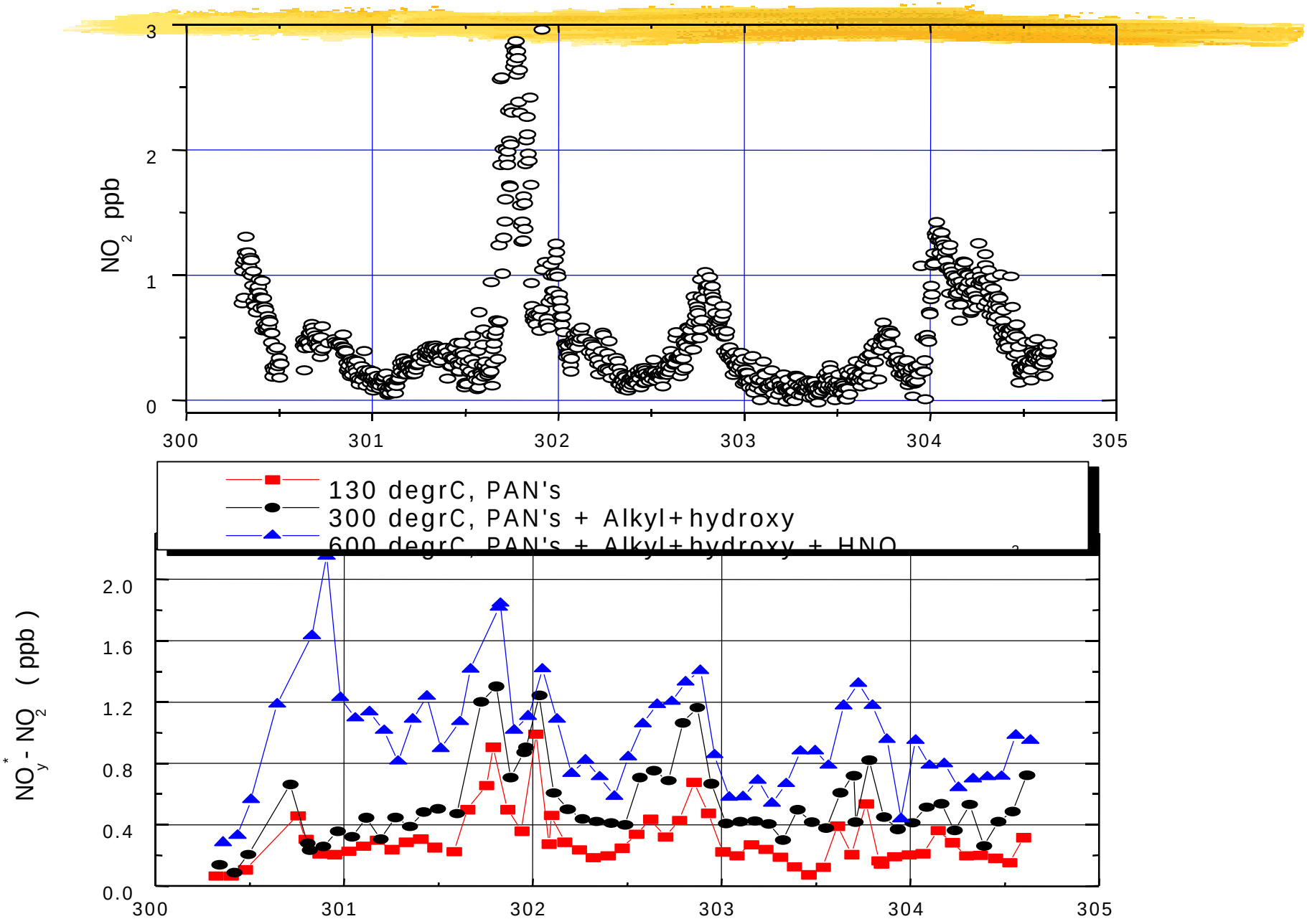
Thermal Spectrum: 991005

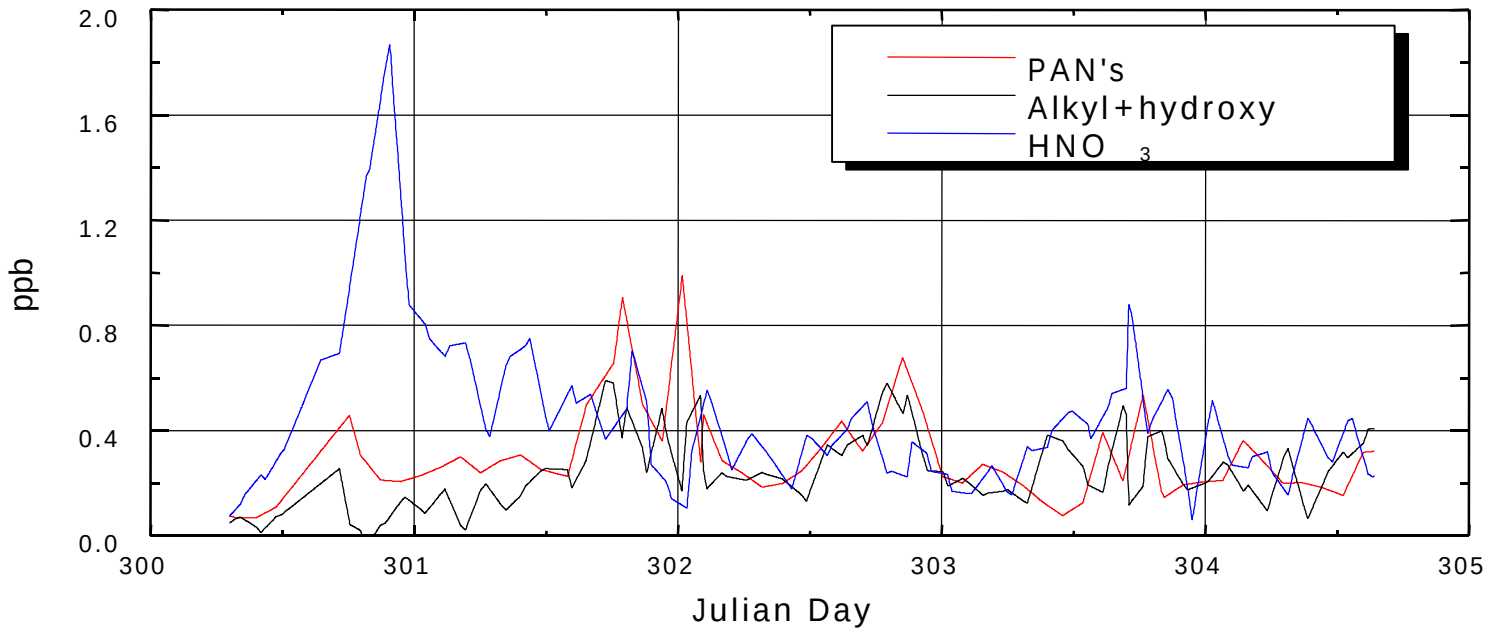


This scan was obtained in the early evening in the peak of the urban plume at Blodgett Forest at the point indicated in the slide below.

991005


130 degrC, PAN's
300 degrC, PAN's + Alkyl+hydroxy
600 degrC, PAN's + Alkyl+hydroxy + HNO3
Temperature Scan
NOy - NOx (ppb)
0
1
2
3
4
277.5
277.6
277.7
277.8
277.9
278.0
278.1
278.2
278.3
Julian Day


3
2
1
0
NO2 ppb
300
301
302
303
304
305
130 degrC, PAN's
300 degrC, PAN's + Alkyl+hydroxy
600 degrC, PAN's + Alkyl+hydroxy + HNO3
2.0
1.6
1.2
0.8
0.4
0.0
NOy* - NO2 (ppb)
300
301
302
303
304
305



A few day sequence of NO_2 (top panel), the sum of NO_y compounds observed at different inlet temperatures, with the NO_2 subtracted (middle panel) and individual classes of NO_y compounds obtained by differencing signals obtained at characteristic temperatures.

Future Work and Applications TD/LIF

Further analysis of the 1999 Blodgett campaign data addressing ozone production, sources of organic nitrates, and modeling the history and processing of the air sampled at the site.

NO_2, organic nitrates, and HNO_3 will be measured at Blodgett Forest for the entire spring-summer-fall season in 2000.

The dual cell technique has been incorporated in an airborne instrument to measure N_2O_5 HNO_3